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ABSTRACT

Ab initio self-consistent-field (SCF) and configuration interaction (CI) calculations which include all single and double excitations from up to three reference functions have been performed for the linear approach ($C_{\infty v}$) of C^+ to H_2 . Both the $^2\Sigma^+$ and $^2\Pi$ surfaces were studied. For the $^2\Sigma^+$ surface the saddle point and barrier height were determined. The computed barrier height of 20 kcal/mole is essentially the same as the empirically corrected barrier of Liskow, et al. The geometry at the saddle point was observed to be very similar to that determined by Liskow, et al. The interaction of the $^2\Sigma^+$ and $^2\Pi$ surfaces was investigated. The location of the intersection leads to the conclusion that in near $C_{\infty v}$ symmetry a low energy path exists by which $CH^+ ^1\Sigma^+$ can be formed, with little or no energy requirement in excess of the endothermicity of the reaction.

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Introduction

The previous theoretical work on the reaction $C^+ + H_2$ by Liskow, Bender, and Schaefer (LBS)¹ mapped out most of the interesting features of the corresponding potential energy surfaces. That initial study used a double zeta (DZ) basis set,² which yielded only qualitative accuracy. In fact, some major discrepancies between the experiments³⁻⁸ and theory were observed.

Pearson and Roueff⁹ showed that using a double zeta plus polarization (DZP) basis set radically changed the surfaces. For the sideways approach of C^+ to H_2 (C_{2v} symmetry), they found that the intersection of the 2A_1 and 2B_1 surfaces was lowered from 10.3 kcal/mole above the reactants energy (DZ) to 15 kcal/mole below the reactants (DZP). This showed a possible low-energy passage to CH_2^+ , which is consistent with the experimental observation that there is no threshold for CH_2^+ formation from $C^+ + H_2$.

The linear approach of C^+ to H_2 to form $CH^+(^1\Sigma^+) + H$ also appears to show a difference between experiment and theory. LBS had a barrier of 28.4 kcal/mole relative to the reactants. They empirically corrected this to 20.1 kcal/mole after noting that the computed endothermicity of the reaction was too large by 8.3 kcal/mole. Based on his interpretation of experimental results, Herbst¹⁰ has concluded that some mechanism which allows the formation of $CH^+(^1\Sigma^+)$ with little to no barrier must exist. The two most likely possibilities are that the barrier is an artifact of the level of calculation used by LBS, or that an avoided crossing in lower symmetry allows the correlation of ground state reactants with ground state products. The nature of this correlation is similar to that discussed by LBS and Pearson and Roueff for the low energy passage for CH_2^+ in C_{2v} symmetry.

The coordinate system used here for the discussion of the linear approach is the same as that of LBS. The separation distance between the two hydrogens is labeled r , while separation between the carbon atom and the nearest hydrogen atom is labeled R . The $^2\Sigma^+$ and $^2\Pi$ potential energy curves, copied from LBS, are shown in Figure 1.* These curves represent different cuts through the surfaces and the point at which the curves cross does not indicate an actual intersection of the $^2\Sigma^+$ and $^2\Pi$ surface, since they have different values of r ; however, they help in an understanding of the possible low-energy passage in low symmetry. The $^2\Sigma^+$ curves is initially repulsive, reaching a maximum at the saddle point and then descending to ground state products, $H(^1S) + CH^+(^1\Sigma)$. The $^2\Pi$ curve, which is initially attractive, becomes repulsive and correlates with excited $CH^+(^3\Pi)$. If the C^+ ion is moved off the linear axis the symmetry is reduced to C_s . One component of the $^2\Pi$ surface becomes $^2A'$ while the second becomes $^2A''$. The $^2\Sigma^+$ curves is now labeled as $^2A'$. In C_s symmetry the $^2A'$ component of the $^2\Pi$ state will not cross the $^2\Sigma^+$ -like $^2A'$, but instead will correlate with the ground state products. Thus for cases of near $C_{\infty v}$ symmetry, we could consider a reaction path which starts on the $^2\Pi$ -like $^2A'$ curve, remains on the adiabatic ground state curve, at the avoided crossing and then follows the $^2\Sigma^+$ -like curve to products. The barrier for this path is given by the height of the avoided crossing above the reactants. An upper bound estimate of this height can be obtained by locating the lowest intersection of the $^2\Sigma^+$ and $^2\Pi$ surfaces in the collinear approach.

$^2\Sigma^+$ Surface

The 9s5p basis set of Huzinaga¹¹ was contracted to double zeta following Dunning.¹² A set of d functions ($\alpha = .75$) centered on the C atom and

* We thank Professor Schaefer for permission to reproduce Figure 5 of ref. 1.

a set of p function ($\alpha = 1.0$) on each H were added to the basis set. This is the same DZP basis as used by Pearson and Roueff.⁹

The entire surface is well described by a single configuration

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 \quad . \quad (1)$$

After performing SCF calculations, a CI treatment including all single and double excitations, CI(SD), was performed. The CI calculations were performed using the programs developed by Shavitt and co-workers.¹³ These CI(SD) calculations yield a classical (no zero point energy) endothermicity of 14.9 kcal/mole. This is in good agreeemnt with an experimental value¹⁴ of 12.5 kcal/mole, and represents a reduction of the error from 8.3 kcal/mole (LBS) to only 2.4 kcal/mole. CI(SD) calculations were performed at the LBS saddle point ($R = 2.51$ and $r = 2.11$ bohr). The barrier height using the DZP basis was found to be 23.4 kcal/mole above the isolated reactants. Applying Davidson's¹⁵ correction for quadruple excitations lowers the barrier to 21.7 kcal/mole, but leaves the endothermicity unchanged.

The saddle point was then determined for the DZP basis at the CI(SD) level. A grid of 6×5 points was used ($R = 2.4, 2.5, 2.525, 2.55, 2.6$; $r = 1.8, 1.9, 2.0, 2.1, 2.2, 2.3$). The saddle point was located at $R = 2.51$ bohr and $r = 1.96$ with a barrier height of 23.1 kcal/mole. The resulting H-H distance is 0.15 bohr shorter than the LBS result (this can, in part, be due to the difference in grid size, 0.1 bohr for here, compared to 0.4 bohr for LBS), but the DZP barrier height is lowered by only 0.3 kcal/mole.

If we follow LBS and substract the error in the endothermicity from the barrier height, the results are essentially the same; 20.1 (LBS) and 19.0 (with Davidson correction) kcal/mole. It seems clear that the LBS predicted

barrier of ~ 20 kcal/mole is correct. This represents a barrier 8 kcal/mole greater than the endothermicity.

$^2\Pi$ Surface

The $^2\Pi$ surface was treated in a different manner than done by LBS. The configuration

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1, \quad (2)$$

is needed to describe $C^+ + H_2$, while

$$1\sigma^2 2\sigma^2 3\sigma 1\pi 4\sigma, \quad (3)$$

is needed to describe $CH^+(^3\Pi) + H$. LBS carried out a single-configuration (2) SCF calculation, followed by CI including all single and double excitation from both reference functions (2) and (3). The CI calculation was iterated several times, each using the natural orbitals from the previous iteration.^{16,17} This was done to improve the orbitals and obtain a smooth curve.

Rather than use a single-configuration SCF and then improve the orbitals at the CI level with natural orbital iterations, we started from a two-configuration SCF (TCSCF), which included configuration (2) plus the configuration

$$1\sigma^2 2\sigma^2 4\sigma^2 1\pi. \quad (4)$$

If we ignore the π electron and consider only the σ electrons, it is known that a TCSCF using configurations (2) and (3) is equivalent to a TCSCF using (2) and (4), the former giving the localized orbital solution, while

the latter gives the delocalized solution. If the π electron is added this is no longer exactly true. Configuration (3) can be coupled to form two doublet functions, one with $3\sigma 1\pi$ coupled to $^1\Pi$, and the other to $^3\Pi$. Since we are interested in the $^3\Pi$ state of CH^+ , the calculation could be designed to produce that. The TCSCF using occupations 2 and 4 will produce a result which is a mixture of $^1\Pi$ and $^3\Pi$ coupled CH^+ . It represents singlet coupling of the CH^+ sigma orbital with the hydrogen atom, followed by coupling the π electron to this to yield an overall doublet. To overcome this problem, all three configurations (2), (3), and (4) were used as reference configurations for the CI and all single and double excitation relative to the three were included. At the products point an SCF calculation was performed using only configuration (3), coupled to $^4\Pi$, followed by CI including all single and double excitation from that configuration. The difference between the $^4\Pi$ CI and the 3-reference $^2\Pi$ CI was only 0.04 kcal/mole. Since the importance of configurations (3) and (4) decreases monotonically from products to reactants, optimizing the orbitals for the weighted average of $\text{CH}^+ ^3\Pi$ and $^1\Pi$ does not add any appreciable error.

At infinite separation between C^+ and H_2 the $^2\Pi$ and $^2\Sigma^+$ states should be degenerate, since both correlate with the ^2P state of C^+ , but as a result of the model used, the $^2\Pi$ energy is actually 0.662 kcal/mole lower. At the products, the $^1\Sigma^+ - ^3\Pi$ separation in CH^+ was computed to be 28.0 kcal/mole, which is in good agreement with the accurate value of 26.3 kcal/mole by Green, et al. As with the endothermicity of the $^2\Sigma^+$ curve, this represents a ~ 6 kcal/mole improvement over LBS.

Surface Intersection

CI (SD) calculations were next performed to locate the intersection of the $^2\Sigma^+$ and $^2\Pi$ surfaces. The lowest intersection point found was at $R = 2.2$ and $r = 2.73$ bohr at 2.43 kcal/mole above the endothermicity of the $^2\Sigma^+$ reaction. Since the equilibrium distance for CH^+ is 2.17 bohr and the line of intersection is very flat from $R = 2.2$ to $R = 2.3$, rising only 0.6 kcal/mole, smaller R values were not considered. For larger CH^+ bond lengths, the crossing takes place at longer H-H distances and higher energy.

If the minimum energy paths for both the $^2\Pi$ and $^2\Sigma^+$ surfaces are considered, they would never approach this region where the surface crossing occurs since these paths involve rather different values of r . However, if a billiard ball model of kinetics is assumed, this region is accessible. If the incoming C^+ ion hits the H_2 molecule nearly end-on and the momentum is transferred to the far hydrogen atom, the H-H bond stretches.

Discussion

In order to put these calculations into perspective we have summarized our CI(SD) results in Table 1. The $\text{CH}^+ \ ^1\Sigma^+ - \ ^3\Pi$ separation is in error by ~ 2 kcal/mole, as is the $^2\Sigma^+$ endothermicity. The $^2\Pi$ reactants are too low by ~ 0.7 kcal/mole. Because of these errors, it is not unreasonable to expect as much as 4 kcal/mole error in the predicted surface crossing.

In Figure 1 we have labeled the endpoints A, B, C, and D. Correcting the known errors represents lowering A by 2 kcal/mole, raising D by 0.7 kcal/mole and lowering B by 4 kcal/mole. If the shape of the curves is held fixed when the endpoints are corrected, the point of intersection would be shifted to lower energy. Reducing the symmetry to Cs by moving off the

$C_{\infty v}$ axis, would also serve to lower the energy of the intersection. Thus these calculations indicate a surface intersection of at no more than 2 kcal/mole, and most likely less than 2, in excess of the endothermicity of the reaction.

Conclusions

The improved calculations presented here for the linear approach of C^+ to H_2 show many of the same qualitative features as those of the Liskow, Bender, and Schaefer surfaces. The barrier on the $^2\Sigma^+$ surface is computed to be ~ 20 kcal/mole or ~ 8 kcal/mole greater than the endothermicity of the reaction. The directly computed surface crossing provides a path for reaction with a barrier of ~ 2 kcal/mole above the endothermicity of the reaction. When the remaining errors are considered, we conclude that a path slightly off $C_{\infty v}$ symmetry would have little or no barrier in excess of the endothermicity of the reaction.

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Table 1.

Summary of linear $C^+ + H_2$ CI(SD) results
(energies in kcal/mole)

$2\Sigma^+$ Saddle point (relative to reactants)

	<u>Computed</u>	<u>Corrected</u>	<u>R (bohr)</u>	<u>r (bohr)</u>
LBS ^a	28.4	20.1	2.51	2.11
this work	23.1	19.0	2.51	1.96

$2\Sigma^+$ Endothermicity

LBS	20.8
this work	14.9
experiment ^b	12.5

Products: $CH^+ 1\Sigma^+ - 3\Pi$ energy difference

LBS	18.3
this work	28.0
Green, ^c et al.	26.3

Reactants: $C^+ + H_2 2\Sigma^+ - 2\Pi$ energy difference

this work	-0.66
correct value	0.00

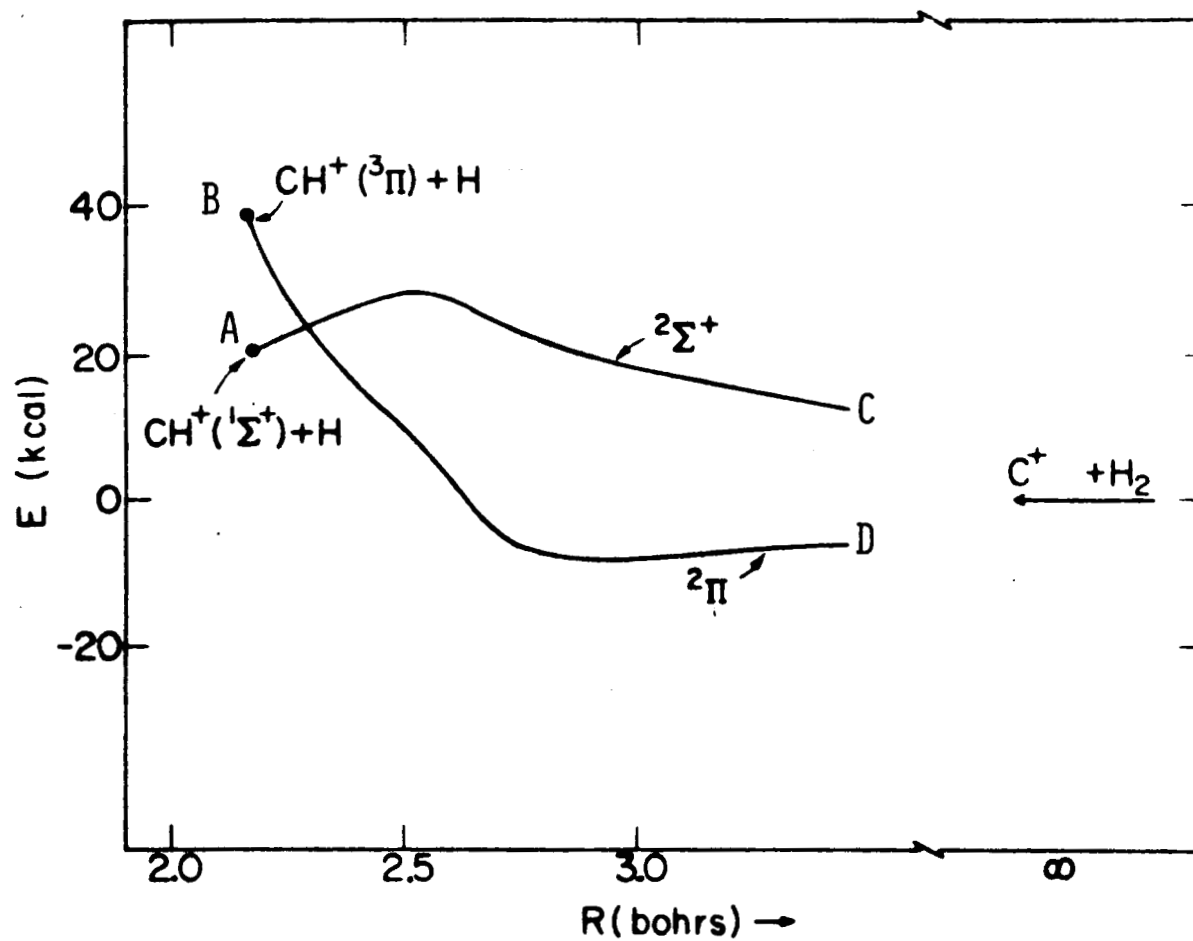
C_{cov} Surface Intersection (relative to products)

<u>Computed</u>	<u>R (bohr)</u>	<u>r (bohr)</u>
2.43	2.2	2.73

^aRef. 1

^bRef. 15

^cRef. 18



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Figure 1. Energy profiles along minimum energy paths for linear $C^+ + H_2 \rightarrow CH^+ + H$, as calculated by Liskow et al. [1].